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Processes for upgrading metallurgical grade silicon to solar grade silicon

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Abstract

The photovoltaic (PV) industry is in rapid growth and a large supply of PV feedstock materials must be provided to maintain this growth. Since silicon is still the dominant material for the fabrication of solar cells, low-cost solar-grade silicon (SoG-Si) feedstock is demanded. The most cost-effective and direct approach for producing SoG-Si is to purify and upgrade metallurgical-grade silicon. Many impurities in MG-Si can be effectively removed through directional solidification of molten silicon. However, the removal of boron (B) and phosphorus (P) by this method is difficult and expensive due to the relatively large distribution coefficients of these elements. Therefore, the elimination of B and P to the levels required for SoG-Si feedstock requires the development of new processes. In the present study, the effect of impurities on the solar cell efficiencies and the impurity contents in silicon materials are studied. The chemical and metallurgical processes that can be applied to purify metallurgical grade silicon to solar grade silicon are reviewed and evaluated. It is shown that under development silicon refining processes are applicable to produce solar grade silicon. However, there are specific challenges for each process and their benefits and risks must be considered for economic production.

Keywords: Metallurgical grade silicon, solar grade silicon, cell efficiency, impurity, refining, directional solidification, slag, leaching, plasma, solvent.

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1. Introduction

Metallurgical grade silicon (MG-Si) is the initial material to produce pure silicon for photovoltaic and electronics applications. It is commercially produced through the reduction of silicon oxide (quartz) with carbon in submerged arc furnaces [1]. An idealized form for the process can be written as:

$$SiO_2 + 2C = Si + 2CO\ (g) \qquad (1)$$

The produced MG-Si is not pure, typically 99.0wt% Si, and it contains impurities such as Fe, Al, Ti, Mn, C, Ca, Mg, B, P and so on. The minimum required purity of silicon for photovoltaic applications is 6N and for silicon wafers used in the semiconductor industry is 9N. The impurities subject to limitations in solar grade silicon (SoG-Si) are the same as in semiconductor silicon [2]. However, the acceptable concentration levels in SoG-Si are substantially higher. The maximum acceptable concentrations of individual impurities in SoG-Si are defined by the conversion efficiency of solar cells. Figure 1 shows the relationship between the cell efficiency and impurity concentration for different silicon grades.

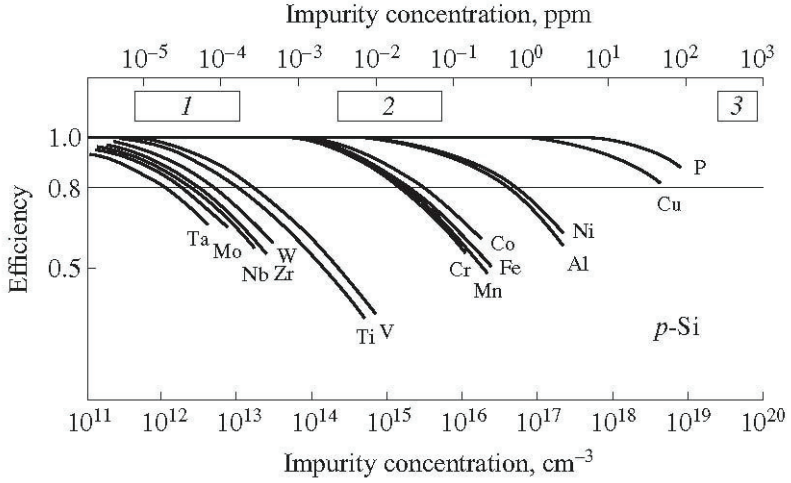

Figure 1: Limits on impurity concentrations in p-type silicon for impurities determining degradation threshold of solar cells [3]:1—Semiconductor-grade; 2—SoG-Si 3—Mg-Si.

The concurrent effect of the increase in the demand for solar silicon and of the costs associated with pure silicon scrap from electronic industry, led the photovoltaic industry to focus the efforts on the development of new production processes dedicated to solar silicon [4] . The development of several alternative routes to the traditional Siemens chemical process of producing pure silicon, was accelerated in the late 1990's. However, the produced polysilicon by this method is still the most used type of silicon feedstock for solar cell manufacturing. In 2009, it had a market share of 97.5% of all the silicon feedstock used for solar cell production, while the rest (2.5%) was represented by upgraded metallurgical grade silicon materials and silicon scrap from the semiconductor industry [5]. The main advantage claimed by manufacturers that developed dedicated metallurgical refining routes concerns the low energy consumption rate. The status of some of the currently operating metallurgical routes of SoG-Si production by producers in Norway, France and China has been recently reviewed by Tranell et al. [6]. According to them, the produced SoG-Si through the combinations of metallurgical methods can provide the required impurity levels for PV applications such as 0.3 ppmw B, 0.6 ppmw P and 1-10 ppmw metals.

In the present study the chemical and metallurgical processes for SoG-Si feedstock production are studied and the challenges in each method is presented and discussed.

2. Chemical processes for silicon purification

In the chemical approach, the production of high purity polycrystalline silicon through reduction and pyrolysis of volatile silicon compounds produced from MG-Si such as $SiHCl_3$, SiH_2Cl_2, SiH_4, $SiCl_4$, $SiHBr_3$,… is carried out. These processes are usually considered as the modifications of the chloride–hydride technology. Traditionally, high pure silicon has been produced through the established, well known Siemens process, which was developed in the 1950s. The production of silicon goes through the gasification of MG-Si, distillation and deposition of silicon [2, 3]. Trichlorosilan ($SiHCl_3$), TCS, is first produced through the interaction of MG-Si with HCl according to reaction (2) under high pressure and temperatures, typically at 500°C and 30MPa. The redistribution of chlorine and hydrogen atoms from $SiHCl_3$ to SiH_2Cl_2 and $SiCl_4$ is then carried out (reaction (3)). The produced dichlorosilane gas is redistributed and distilled to monochlorosilane gas, which again is transformed to silane gas according to reactions (4) and (5). Through distillation, diboride and other impurities are removed. This is an important step in the process as B is a harmful element disturbing the electrical properties of the final material.

$$5(MG\text{-})Si + 16\ HCl = 4\ HSiCl_3 + 6H_2 + SiCl_4 \quad (2)$$
$$2\ SiHCl_3 = SiH_2Cl_2 + SiCl_4 \quad (3)$$
$$2\ SiH_2Cl_2 = SiHCl_3 + SiH_3Cl \quad (4)$$
$$2\ SiH_3Cl = SiH_2Cl_2 + SiH_4 \quad (5)$$

The pure TCS gas is decomposed to pure Si on a U-shaped filament according to reaction (6), where the produced HCl is re-used in the initial process step [3]. This chemical vapor deposition (CVD) reaction takes place at 1000-1100°C and the filament is heated with ohmic energy.

$$HSiCl_3 + H_2 \rightarrow Si(s) + 3HCl \quad (6)$$

Using silane (SiH_4) instead of TCS ($SiHCl_3$) during decomposition simplifies the process and in this process SiH_4 is decomposed according to the following reaction at 800-1000°C [2]:

$$SiH_4(g) = Si + H_2(g) \quad (7)$$

Using silane instead of TCS during decomposition simplifies the process due to the lower boiling point of silane compared to other liquids in the process, as hydrides, chlorides of boron, phosphorous and arsine. A very pure gas is hence obtained, with less energy consumption. Moreover, the highly corrosive chlorine-components are not present, which simplifies the material choices of the process equipment. Using a Fluidized Bed Reactor (FBR), instead of a U-shaped filament during decomposition, increases the decomposition surface and hence, the total production rate [7]. With FBR process, SoG-Si is produced at a lower cost, and using much less energy than the traditional Siemens method for converting silane gas to high purity silicon. Unlike the Siemens process which requires the breaking of polysilicon rods, FBR granular is harvested in a ready to use form. In addition, the FBR process is continuous, which is an advantage over the Siemens batch process [7]. It goes without saying that this can be a disadvantage with regard to the more complicated process control of a fluidized bed reactor.

The major problem of the chemical route is that it involves the production of chlorosilanes and reactions with hydrochloric acid. In addition to being toxic, these compounds are corrosive, causing irritations of the skin and mucous membranes. Moreover, their handling also requires the utmost care, since they are explosive in the presence of water and hydrochloric acid. Chlorine emissions in polycrystalline silicon production by the chemical route are estimated to amount to 0.002 kg of chlorine per square meter of cell. Controlling this emission is important because chlorine is denser than air, which accelerates the poisoning process [4]. These problems together with relatively high energy consumption of SoG-Si production through the chemical route have been the driving force for the development of metallurgical processes for SoG-Si feedstock production in the recent years.

3. Metallurgical processes for silicon purification

In SoG-Si production through metallurgical approach, MG-Si is purified by the combination of metallurgical techniques. An overall sketch of the metallurgical route from quartz to SoG-Si is shown in Fig. 2. As observed, directional solidification is a key process step for the metallurgical route. This is due to the large segregation of the impurities between the liquid and solid silicon phases during solidification. Boron and phosphorus, which are always present in the MG-Si (produced from ordinary raw materials) has relatively large segregation coefficients in directional solidification, which are 0.8 and 0.35, respectively [8, 9]. Therefore, the removal of these impurities by directional solidification is difficult and cost ineffective. Hence, the application of other metallurgical techniques dedicated mainly to remove B and P is necessary to produce a high-quality silicon (HQ-Si) devoid of B and P prior to directional solidification.

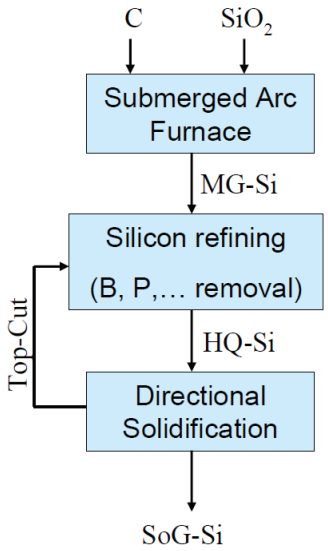

Figure 2: Overall sketch of the SoG-Si production from quartz through metallurgical route.

Although many research works have been done on silicon purification with main focus on B and P removal, a few full metallurgical processes have been developed. In *Elkem Solar* process in Norway, MG-Si is refined through slag treatment followed by acid leaching and directional solidification [10]. In French *Photosil process*, MG-Si is refined through two steps segregation refining, plasma purification, post plasma segregation and directional solidification [11]. In China, a range of companies have

developed and are currently operating industrial metallurgical processes for SoG-Si production. They apply gas blowing, slag refining, acid leaching, vacuum refining and directional solidification to produce SoG-Si [6]. In the *NS Solar Material (NSSM) process* in Japan, MG-Si is first refined by oxidation for B removal, then it is vacuum treated for P removal, and directional solidification is applied to remove the metal impurities [12]. *Fesil Sunergy* process in Norway is based on the use of pure raw materials (low in B and P) application for SoG-Si production. In this process high purity silicon carbide is first produced and then used for the carbothermic reduction of high purity quartz in electric arc furnace. The obtained silicon is then refined through particle settlement, filtration, and oxygen purging and solidification [13]. Selected refining processes, which are currently used in the above mentioned processes, are studied as follows.

3.1. Directional solidification

Directional solidification of silicon as mentioned before is a key process step in the SoG-Si production through the metallurgical route. Significantly small segregation coefficient of many impurities (except B and P) between the solid and molten silicon provides proper conditions for silicon refining by directional solidification [8, 9]. Directional solidification of the melt takes place when the removal of both the heat necessary for the melt to cool down to the solidification temperature and the latent heat generated at the solidification front due, occurs along a single direction [14]. Directional solidification is usually performed along the vertical direction, i.e. from the bottom to the top of the ingot. With regard to the uniqueness of directional solidification on removal a wide range of impurities from silicon, it is expected that this process will continue to be a part of the best developed process for SoG-Si production.

3.2. Slag refining

Slag refining technique is a process candidate for mainly B removal in which the boron impurity in molten silicon is oxidized and removed by a molten silicate slag. The related chemical reaction can be written as:

$$[B]_{Si} + SiO_2 = (B_2O_3) + Si \qquad (8)$$

The thermodynamics of B removal by silicate slags has been studied through several works and the distribution coefficient of B between slags and molten silicon ($L_B = \frac{(\%B)_{slag}}{[B]_{Si}}$) has been measured. It has been observed that L_B decreases with increasing the basicity of CaO-SiO_2 slags and a minimum of $L_B \approx 2$ is obtained for $CaO/SiO_2 = 0.85$, while L_B is increased with increasing the slag basicity [15]. Relatively lower L_B have been reported for the same slag system in the other studies [16, 17]. Reported measured L_B values in literature for different slag compositions show that the majority of them are in the range between 0.5 and 3.5 [15, 16, 17, 18, 19]. The distribution coefficient of B is minimally affected by the refining temperature and small increase of L_B with increasing temperature has been reported [16]. Both the research works and also the developed Elkem Solar process indicate that slag refining is efficient for B removal. It is worth mentioning that slag treatment may also remove some other impurities. For instance, there is no specific process step for phosphorus removal in the Elkem solar process; the P elimination can take place likely to some extent through the slag refining.

The application of slag refining for silicon purification has its own advantages and disadvantages. The slag refining process is a kind of well known batch process in which solute and even solid impurities in a molten metal are removed, and it is used in many metallurgical processes such as clean steel production. The process operation may be not complicated and can be done in large scale in high capacity metallurgical vessels. However, responding specific challenges is crucially important in this process such as preparation of clean slag with ultimately low concentrations of B. Moreover, with regard to the equilibrium thermodynamics (L_B) in slag refining process, the removal of B from the usual concentrations in MG-Si i.e. 20 ppmw to below 0.5 ppmw requires large volume of slag compared to the silicon, or slag treatment in sequences. The kinetics issues in slag refining of silicon has not been studied extensively and the parameters affecting the process rate are not well known.

3.3. Acid leaching

Many metallic elements such as Fe, Al, Ti, Ca, Mn, Mg, Sb, Sn, Zn, Cu, Au and Ni have high segregation coefficients in silicon. Thus, during solidification of molten MG-Si, a major portion of these impurities should precipitate at grain boundaries or at interstitial positions in polycrystalline silicon. Hence, acid leaching of MG-Si dissolves the impurities located at the grain boundaries of silicon, while the silicon matrix is not dissolved. Therefore, the silicon purity can be improved by leaching process. In practice, it would be more beneficial to add Ca to the molten MG-Si and solidify the melt which causes the precipitation of $CaSi_2$ at the grain boundaries as the dominant present phase [20]. Other impurities are concentrated as small grains in the calcium disilicide phase. The reaction of $CaSi_2$ with HCl in acid leaching gives:

$$3CaSi_3 + 6HCl + 3\ H_2O = Si_6H_6O_3 + 3\ CaCl_2 + 3H_2 \qquad (9)$$

The lumps of calcium-containing silicon disintegrate during leaching into silicon grains less than about 2 mm and a fine-grained material that is easily separated from the silicon grains by washing. In the original leaching alloy most of the impurities occur as very small grains in the calcium disilicide phase. Even if they are not dissolved during the leaching, they are washed away with the fines. Some impurity particles stick to the silicon crystals and are removed in a second leaching by hydrofluoric acid and some oxidizing agent [20]. The removal efficiency of the impurities is in a range from 70 to around 90 %. However, the treatment by leaching is not effective for B, C and O. Addition of Ca to the silicon alloy allows to remove P by a factor of 5 down to relatively low concentrations less than 5 ppmw [21]. The effect of various parameters such as leaching agent, temperature, particle size on leaching efficiency have been studied [22, 23, 24] and all these parameters may affect the extents of impurities elimination.

3.4. Vacuum refining

Vacuum distillation technique for the purification of molten metals and alloys has been developed mainly in the last century. Vacuum refining has also been applied in laboratory scale to remove particular impurities from silicon such as phosphorus through several studies. As mentioned above, this method is currently applied for SoG-Si in Chinese and Japanese companies. The difference in the vapour pressures of the liquid silicon and the volatile impurities is the basic principle of vacuum refining. The relationship between the saturated pressure and temperature for some pure elements is illustrated in Fig. 1. Based on the Hertz-Langmuir-Knudsen equation for the evaporation of substances in vacuum, Olette [25] developed a kinetic volatility criterion for vacuum refining. This criterion for the monatomic evaporation of impurity *i* in dilute solution with silicon solvent can be written as:

$$\alpha = \frac{\gamma_{\mathrm{i}}^{\mathrm{o}} p_{\mathrm{i}}^{\mathrm{o}}}{p_{\mathrm{Si}}^{\mathrm{o}}} \left(\frac{M_{\mathrm{Si}}}{M_{\mathrm{i}}} \right)^{1/2} \qquad (10)$$

where p_{Si}° and p_i° are the vapour pressures of pure silicon and impurity at a given temperature, and γ^{o}_i is the Henrian activity coefficient of the impurity. M_{Si} and M_i are the atomic weight of silicon and impurity, respectively. The magnitude of α from one solute to another indicates relative rates of refining when monatomic evaporation controls rate of refining. If $\alpha>1$, the impurity can be removed almost completely from silicon. If $\alpha<1$, the impurity cannot be removed and the silicon evaporation rate is greater than the impurity. Obviously, $\alpha=1$ shows that both silicon and the impurity are evaporated with equal rates.

The application of vacuum induction melting for the purification of metallurgical grade silicon (MG-Si) has been investigated through several experimental works and they were reviewed recently by authors [26]. Phosphorus is the main element removed through vacuum distillation due to its much higher vapour pressure which gives large α-value. However, the removal of other volatile impurities such as Al, Ca, Mg, Na,… occurs in vacuum refining. It has been recently shown by authors that the chemical composition of the silicon melt affects the P removal rate and it is faster from cleaner melts [27].

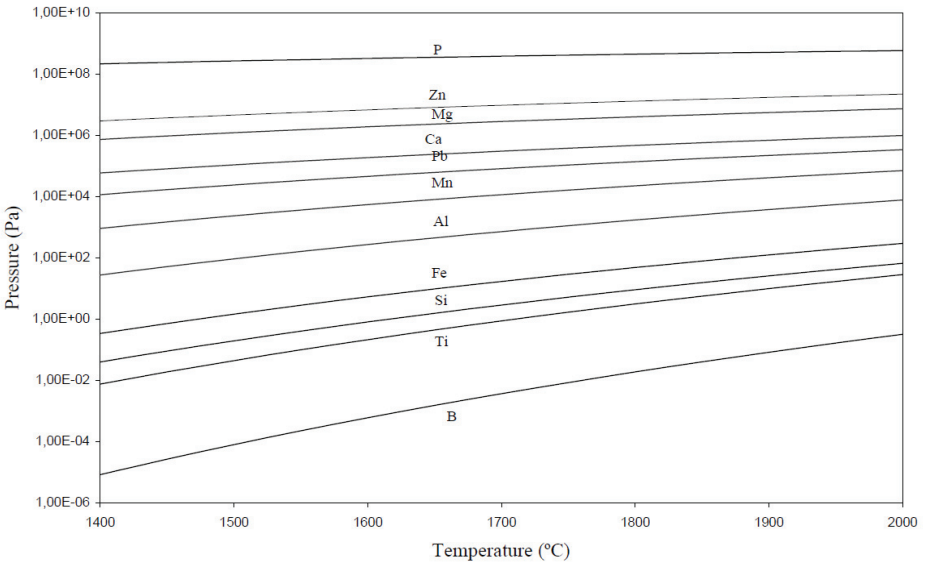

Figure 3: The changes of the standard vapour pressure of pure substances with temperature calculated from the reported thermodynamic data [27].

Vacuum refining is a process with particular advantages which make this technique as a successful process candidate for SoG-Si production in combination with other processes for the removal of non-volatile elements such as B. The process is not complicated and its control is not difficult. In vacuum refining, no other material except the holding crucible is in contact with the silicon melt which prevents the introduction of impurities during the refining. Since silicon is not conductive, the application of vacuum induction technique can be the best solution with using high purity graphite crucible, which is available in the market. The process can be done combined with directional solidification in a single furnace, which is more energy efficient.

3.5. Plasma refining

Plasma refining is a technique that has been used for the removal of B from silicon. The removal of boron from metallurgical-grade silicon was investigated by Suzuki et al. [28] with applying an Ar/H_2O plasma treatment. They reported concentration changes of boron in MG-Si from 35.7 to 0.4 ppmw within 25 minutes of refining time. Within the framework of the NEDO program, Japanese groups studied boron removal and developed a purification process combining arc plasma, electron beam, and directional solidifications. Plasma treatment used water as the reactive gas to remove boron, an electron beam was used to remove phosphorus under vacuum, and two directional solidification steps allowed metallic impurities to be removed. The amount of silicon treated during these studies reached 300 kg per batch [29]. The French Photosil process is the other process with progresses toward industrial production [30] which makes use of plasma refining as a key step for B removal. In this process the dissolved B in liquid silicon is converted to boron oxides such as BO, B_2O, BO_2, B_2O_2, B_2O_3 or boron hydrates such as BHO, BH_2, BHO_2, BH_2O_2, BH_3O_3, $B_2H_4O_4$, $B_3H_3O_3$, $B_3H_3O_6$, which are volatile compounds [31] compared to liquid silicon.

Although silicon refining has shown good results in B removal, there are particular cases to be considered. The process seems to be complicated from technology and process control points of view. The limitation in boron volatilization is due to the formation, at high oxygen flow rate, of a silica layer at the surface of the molten silicon, which results in a dramatic drop of the volatilization rate [32]. The silicon yield in plasma refining is not clear and it might be high due to the high temperature on the silicon melt surface.

3.6. Solvent refining

Solvent refining is a purification process in which MG-Si is dissolved in a melt and then it is recrystallized in more pure form a supersaturated melt. The refining efficiency depends on the segregation behavior of different elements in solid silicon and the liquid phase. Solvent refining of silicon through using Si-Al melts has been studied in the recent years in Japan [33, 34, 35] and it has been indicated that the segregation coefficient of the impurities between solid silicon and liquid Si-Al melts is considerably smaller than that between solid and liquid silicon. For instance, the segregation coefficient of B in Si is 0.8 at the silicon melting point (1414°C), whereas it is around 0.2 when silicon is solidified from Si-Al melt at 1000°C. For phosphorus the segregation coefficient is 0.06 when silicon is solidified from Si-Al melt at 700°C, which is much less than 0.35 for recrystallization from liquid silicon [**Feil! Bokmerke er ikke definert.**]. Solvent refining of silicon through silicon recrystallization from Si-Ni melts has also been studied recently and it has been shown that impurities can be effectively removed from silicon through solvent refining by Si-Ni melts [36].

Solvent refining using Si-Al and Si-Ni melts as the impurity trappers has shown high impurities removal efficiencies mostly above 90%. This may indicate that solvent refining is a promising method. However, there are particular challenges to utilize this method in industrial scale. Preparation of high purity alloying metals (such as Al and Ni) with reasonable price is a case. The application of the produced impure metal/alloy through solvent refining which carries the impurities of the MG-Si is also another issue. If it is recycled in plant, it requires extra refining processes which are cost effective to the final purified silicon product. The separation of recrystallized silicon from the refiner melt, or from the solidified melt containing Si crystals is also a challenge. The separation may be not perfect with high silicon yield. It can also introduce impurities to the refined silicon, in particular if crushing is needed.

4. Concluding remarks

- Although the produced SoG-Si through chemical routes is still the dominant feedstock material for PV industry, metallurgical processes for SoG-Si feedstock production have had significant progress in the recent years.
- Production of SoG-Si through metallurgical approach combines a number of refining steps in addition to refining directional solidification.
- All the pyro- and hydrometallurgical refining methods have specific advantages and disadvantages and they face particular challenges.
- Operation and process control, energy consumption, impurity removal efficiency, silicon yield, pure refiner material preparation, recycling or selling of polluted refiner material, and separation of purified silicon from refiner material are the challenges in the metallurgical techniques for silicon refining.

Acknowledgements

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